

RAMAN SPECTROSCOPIC STUDIES OF
CH₃- AND CD₃-(4-TERT-BUTYLPYRIDINE)-
BIS(DIMETHYLGLYOXIMATE)COBALT (III) COMPLEXES:
REASSIGNMENT OF THE METHYL-COBALT STRETCHING VIBRATION

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ABSTRACT

By comparing the Raman spectra of the methyl-d₀- and methyl-d₃-(4-tert-butylpyridine)cobaloxime¹ complexes, a number of bands were observed to shift due to the isotope effect. Bands appearing at 2900 cm⁻¹ in the spectrum of the lighter molecule and at 2109 cm⁻¹ in the spectrum of the C-deuterated species are assigned respectively to the axial methyl C-H and C-D symmetric stretches; the bands at 1172 and

898 cm^{-1} , to the axial CH_3 and CD_3 symmetric deformations; and the bands at 506 and 478 cm^{-1} , to the Co-CH_3 and Co-CD_3 stretches. The new assignment of this fundamental may prove useful in understanding the reactions of methylcobalamin and its analogues.

INTRODUCTION

Compounds containing cobalt bonded to methyl, such as methylcobaloximes and the coenzyme methylcobalamin, are of immediate interest because of their ability to methylate heavy metals such as mercury and platinum.² The fact that the cobaloximes have been shown to mimic the reactivity of methylcobalamin, as well as their relative ease of synthesis, makes them convenient model compounds.³ Figure 1 depicts the basic structural features of these compounds. In this research, the cobaloximes studied were those with $\text{R} = \text{CH}_3$ or CD_3 and $\text{B} = 4\text{-tert-butylpyridine}$ as axial ligands above and below the plane of the bis-glyoximate ring.

It is commonly believed that the fundamental step in the mechanism of many of these metal methylations involves cobalt-methyl bond breaking.² Hence a study of this process would be of central interest. One possible approach to investigating this mechanism directly would be to monitor the band intensity of the methyl-cobalt stretch as the reaction proceeded. Thus, the purpose of this work is to elucidate the vibrational

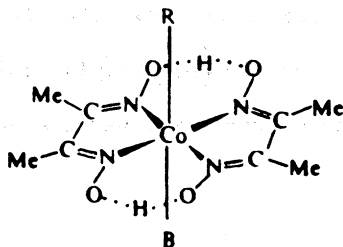


FIG. 1. Basic structural features of cobaloximes. [R = CH₃ or CD₃; B = 4-tert-butylpyridine.]

spectra of model cobaloximes with particular emphasis on the identification of the cobalt-carbon stretching vibration.

Previous researchers have assigned the Co-CH₃ stretching vibration in methylcobaloximes to an infrared band observed near 325 cm⁻¹, and have probed the effect on this peak of axial substitution trans- to the Co-C bond.^{4,5,6} Such an assignment seems equivocal in light of other documented evidence about metal-carbon stretching bands for other complexes with methyl ligands. For example, in Hg(CH₃)₂ and in cis-Pt(CH₃)₂(PMe₃)₂, this vibration is observed in the infrared at 522 and 540 cm⁻¹, respectively.^{7,8} Furthermore, by comparison of the infrared spectra of L₄CoCH₃ and of L₄Co (where L = Me₃P), one can readily assign the Co-C stretching vibration in the former complex to a weak band at 431 cm⁻¹.⁹ Finally, for L₃CoCH₃ (where L = Ph₃P), deuteration of the methyl group shifts the Co-C stretch from 465 to 430 cm⁻¹.⁵ In an attempt to resolve the present

uncertainty in the assignment of the Co-CH₃ stretch, the Raman spectra of methyl(4-(tert-butylpyridine)cobaloxime and its deuterio-methyl analog were examined and compared.

EXPERIMENTAL

Methyl(4-tert-butylpyridine)cobaloxime and its CD₃ analog were prepared by literature methods.¹⁰ The methyl compound was characterized by elemental analysis at Galbraith Laboratories, Knoxville, TN. (Calcd. for C₁₈H₃₀N₅O₄Co: C, 49.20%; H, 6.38%; N, 15.68%; Co, 13.41%; found: C, 48.94%; H, 7.04%; N, 15.68%; Co, 13.33%.)

Mass spectra of the two compounds were run on a Hitachi Perkin Elmer RMH-2. For the CH₃ complex, only one ion at m/z = 439 was observed in the 350-500 mass region, while for the CD₃ species the only ion in this region was at m/z = 442.

Laser Raman spectra were obtained under ambient conditions on a Spex 1401 double monochromator equipped with an RCA 31034 photomultiplier tube. (The detector was operated at 1620 V in the photon counting mode.) The exciting radiation was the 514.5 nm line of Spectra Physics (Model 165-03) argon ion laser. Laser power at the sample was about 350 mW. The finely ground, polycrystalline sample was gently packed into a 5 mm o.d. nmr tube. The tube was then spun during data collection to minimize sample decomposition in the laser beam. The spectra were scanned at approximately 7 cm⁻¹ resolution from

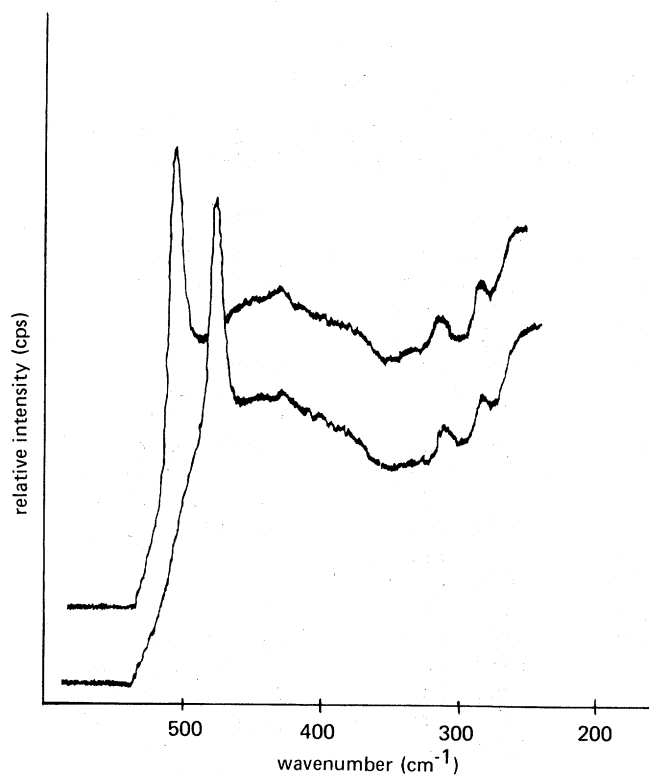


FIG. 2. Raman spectra of CH_3 - and CD_3 -(4-tert-butylpyridine)-cobaloximes: $[\text{Co}-\text{CH}_3 \text{ stretch} = 506 \text{ cm}^{-1}$; $\text{Co}-\text{CD}_3 \text{ stretch} = 478 \text{ cm}^{-1}$.

$200 \text{ to } 3100 \text{ cm}^{-1}$ at a speed $0.83 \text{ cm}^{-1}/\text{s}$ and a pen period of 2.5 s. Figure 2 presents the spectra of the complexes in the region between $200 \text{ and } 600 \text{ cm}^{-1}$. Table 1 gives the recorded peaks with their relative intensities and tentative assignments.

DISCUSSION

As can clearly be seen from the Table, the Raman spectra of the two compounds are virtually identical except for three

TABLE 1

Observed Raman Frequencies and Tentative Band Assignments
for CH₃- and CD₃-Cobaloxime (cm⁻¹).

CH ₃	CD ₃	Assignment ^a
260 (1) ^b	260 (1) ^b	Co-N str (py) ?
285 (1.5)	285 (1.5)	--c
312 (1)	312 (1)	--
427 (0.5)	426 (0.5)	Co-N ₄ sym str
-	478 (10)	Co-CD ₃ str
506 (10)	-	Co-CH ₃ str
586 (1)	587 (1)	C=N-O def (dmg) ?
731 (3)	730 (3)	out-of-plane CH def (py)
807 (2)	811 (2)	skel def (dmg) ?
-	898 (6)	axial CD ₃ sym def
900 (1.5)	900 (1)	--
941 (1)	940 (1)	--
997 (1.5)	996 (1.5)	--
1007 (1.5)	1007 (1.5)	sym ring breathing mode (py)
1024 (3)	1024 (3)	in-plane C-H def (py)
1064 (3)	1064 (3)	N-O str
1135 (2)	1135 (2)	C-CH ₃ str (dmg)
1145 (2)	1149 (2)	--
1172 (2)	-	axial CH ₃ sym def
1202 (1)	1202 (1)	in-plane CH def (py)
1234 (1.5)	1234 (2)	N-O str
1360 (5)	1359 (4.5)	C-C str (dmg)
1390 (1)	1390 (1)	CH ₃ sym def (dmg)
1488 (9)	1488 (9)	N-O-H def
1575 (1)	1575 (1)	C=N str
1615 (2)	1615 (2)	C=N str; ring str (py)
-	2109 (1)	axial CD ₃ sym str
2900 (2)	-	axial CH ₃ sym str
2918 (4)	2918 (3.5)	CH ₃ sym str (dmg)
3076 (0.5)	3076 (0.5)	CH str (py)

^a Based in part on ref. 5-6,11-14. Abbrev.: sym = symmetric; str = stretch; def = deformation; dmg = dimethylglyoxime; py = pyridine; skel = skeletal.

^b Numbers in parentheses represent peak intensities (on a scale from 0-10) relative to the strongest band.

^c Assignment uncertain.

pairs of isotopically shifted bands which can be assigned to vibrations associated with the axial methyl moiety attached to the metal. In particular, the band at 2900 cm^{-1} in the light molecule is shifted to 2109 cm^{-1} by deuteration. These peaks are clearly due to the CH_3 and CD_3 symmetric stretching modes of the axial methyl group. (The corresponding asymmetric modes are generally too weak to observe in the Raman spectrum of methyl-containing compounds). This assignment is corroborated by the fact that the frequency shift calculated by Krimm's approximate isotopic frequency rule¹⁵ (0.715) agrees quite closely with the observed value of 0.727. The two bands observed at 1172 and 898 cm^{-1} , respectively, in the spectra of the CH_3 and CD_3 species, are associated with the symmetric deformations of the axial methyl moieties. Again, the calculated frequency shift¹⁵ (0.769) and the observed shift (0.766) are nearly equal.

The last pair of bands in the Raman spectra of the CH_3 - and CD_3 -(4-tert-butylpyridine)cobaloxime complexes (Fig. 2) which exhibit an isotopic shift appear at 506 and 478 cm^{-1} , respectively. These are too low in frequency to be assigned as methyl rocking motions; the remaining normal vibration of the methyl group itself, the methyl torsion, is typically a very weak, broad feature which absorbs below 250 cm^{-1} . The only other vibrations which are likely to be effected by deuterium substitution at the methyl carbon are the Co-C stretch and the

C-Co-N₄ bending motion. These two fundamentals will exhibit significant isotopic frequency shifts if they are strongly kinematically coupled to the vibrations of the methyl group. Such mechanical coupling is commonplace between the symmetric methyl deformation and the C-Y stretching vibrations, where Y is the atom to which the methyl group is sigma bonded.

To a good approximation, the frequency $\tilde{\nu}$ of a stretching vibration is proportional to the square root of the force constant K and inversely proportional to the square root of the reduced mass μ of the two atoms connected by the bond:⁷

$$\tilde{\nu} \propto \sqrt{K/\mu} \quad (1).$$

If one assumes for the moment that the Raman bands at 506 and 476 cm⁻¹ are indeed the CH₃-Co and CD₃-Co stretches and if one treats the two methyl groups as point masses of 15 and 18 amu, respectively, then because K is virtually unchanged by isotopic substitution, one can use equation (1) to show that the frequency ratio of these two stretching vibrations is inversely proportional to the square root of the respective reduced masses:

$$\frac{\tilde{\nu}_a}{\tilde{\nu}_b} = \frac{\sqrt{\mu_b}}{\sqrt{\mu_a}} \quad (2)$$

The ratio of the two observed frequencies, 0.93, compares favorably with the value of 0.94 calculated for these bands by equation (2). Thus, it seems reasonable to assume that these two Raman features represent the Co-CH₃ and Co-CD₃ stretching vibrations.

These methyl cobaloxime complexes have a broad, intense UV-visible absorption band centered near 440 nm, which has previously been assigned as the Co-CH_3 charge-transfer band¹⁶. Because this band system partially overlaps the 514.5 nm laser line used for Raman excitation, some resonance enhancement of the Raman intensities of the vibrational modes associated with the Co-CH_3 chromophore is likely. Such an effect would explain why the two bands here assigned to the cobalt-methyl stretching vibrations are the most intense in the observed Raman spectra and thus lend further credence to the present assignment. On the other hand, because this normal vibration often leads to rather weak infrared band intensities (cf. the spectral data in refs. 6, 7, for example), these bands may easily be obscured by other stronger bands in the same region of the infrared spectra of methylcobaloximes⁴⁻⁶ and thus not readily observed.

The infrared band observed at 327 cm^{-1} in methyl-(pyridine)cobaloxime,⁴⁻⁶ which shifts to 321 cm^{-1} when the methyl group is deuterated,⁵ should then be attributed to a C-Co-N deformation mode. This may account for the smaller observed isotopic shift (1.9% in this case, compared to 5.5% for the stretching vibration).

Polarized infrared spectra of methyl(imidazole)cobaloxime provides another bit of evidence supporting these hypotheses. When single crystals of this compound are oriented such that

the Me-Co-Im axis is perpendicular to the plane of the electric vector of plane polarized infrared radiation, very little absorption intensity is predicted for the Co-C stretching vibration. By contrast, the transition moment of the C-Co-Im bending mode will be more nearly parallel to the plane of the electric vector and should show normal intensity in the observed spectrum. Because a band is observed at 325 cm^{-1} in the polarized infrared spectrum of oriented methyl(imidazole)-cobaloxime for either orientation of the polarizer perpendicular to the C-Co-Im axis, this band cannot be due to the stretching motion of the Co-C bond.¹⁷

Finally, the latter normal mode is symmetric with respect to the C_2 axis of the complex, and would generally be expected to exhibit greater Raman than infrared intensity. The skeletal bending vibration, however, is antisymmetric to the symmetry axis and should show relatively stronger infrared absorption than Raman scattering.

In summary, the present Raman data leads to a reassignment of the Co-CH₃ stretching vibration to an intense Raman band at 506 cm^{-1} , which is not observed in the infrared.⁴⁻⁶ Because the nature of the ligand trans- to the methyl ligand may affect this vibration,¹⁸ compounds previously studied only by infrared⁶ should be reexamined by Raman spectroscopy to verify whether such an effect can be observed for these species.

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